

**UNITED STATES PATENT APPLICATION**

**OF**

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**AND**

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**FOR**

**METHODS FOR RELAXING AND RE-WAVING HAIR COMPRISING AT LEAST  
ONE REDUCING AGENT AND AT LEAST ONE HYDROXIDE COMPOUND**

05725.0639-00

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[004] Generally, hair relaxing processes are chemical processes which may alter the aforementioned disulfide bonds between polypeptides in hair fibers and may form lanthionine residues  $[S[CH_2CH(NH-)(CO-)]_2]$ . Thus, the term "lanthionizing" is used when one skilled in the art refers to the relaxing of keratin fibers by hydroxide ions. "Lanthionizing," as used herein, refers to the formation of at least one

“Relaxation” and “relaxing,” as used herein, includes any level of relaxing, for example, from slight relaxing to straightening.

[006] The reaction with the alkaline agent is normally initiated by available hydroxide ions. As used herein, "available hydroxide ions" are hydroxide ions which are available for lanthionization. Not to be limited by theory, there are two reaction sequences that are predominantly used in the art to explain the disruption of the disulfide bonds in hair fibers by available hydroxide ions. Both of these reaction sequences result in lanthionine residue formation. Generally, hydroxide ions initiate a reaction in which a cystine cross-link ( $-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$ ) is broken and a lanthionine cross-link ( $-\text{CH}_2-\text{S}-\text{CH}_2-$ ) is formed. The lanthionine cross-link is shorter than a cystine cross-link by one sulfur atom, and thus the net effect of the reaction is to reduce the distance between polypeptides. Amino acid analysis indicates that from 25 mole% to 40 mole% of cystine residues are converted to lanthionine residues.

[007] One reaction sequence comprises at least one bimolecular nucleophilic substitution reaction wherein an available hydroxide ion directly attacks the disulfide

[008] Hydroxide-containing alkaline agents also have other advantages. For example, alkaline agents, such as sodium hydroxide and guanidine hydroxide, do not have a highly objectionable odor or cause such an odor on treating the hair. Further, hydroxide-based straighteners generally have relatively fast processing times and good straightening of naturally curly or kinky hair. Additionally, the achieved straightening effect is more durable; *i.e.*, less likely to revert to a curly state after shampooing and exposure to the elements than is hair straightened with some other straighteners.

[009] Despite these advantages, certain hydroxide-containing alkaline agents may have disadvantages. These disadvantages may be heightened when the hydroxide-containing alkaline agent is sodium hydroxide. Specifically, the causticity of sodium hydroxide can adversely affect the condition of the hair, for example, leaving it in a brittle state and harsh to the touch. Additionally, prolonged or unnecessary exposure of hair to such a strong alkali can weaken, break and dissolve the hair. The mechanical properties of hair that has been lanthionized using hydroxide ion generating compositions demonstrate that, while the hair may not be significantly weaker due to the reduction in space between polypeptides (and in fact may have a high yield force), the hair may have a lower elongation before breaking. This "brittleness" of high yield force coupled with low elongation and inherently weaker points (where the hair had natural twists) can lead to breakage during grooming. Further, in some instances, such a strong alkali can discolor the natural color of the hair. For example, the tone of natural brown hair may be reddened and natural white or grey hair may be yellowed. Further, the natural sheen of the hair may be delustered.

[010] Most frequently, commercial relaxing compositions are in the form of gels or emulsions that contain varying proportions of strong water-soluble bases, such as sodium hydroxide (NaOH), or of compositions that contain slightly-soluble metal hydroxides, such as calcium hydroxide (Ca(OH)<sub>2</sub>), which can be converted *in situ* to soluble bases, such as guanidine hydroxide. Traditionally, the two main hair relaxers used in the hair care industry for generating hydroxide ions are referred to as "lye" (lye = sodium hydroxide) relaxers and "no lye" relaxers.

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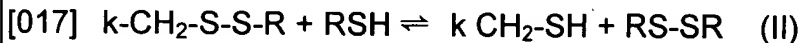
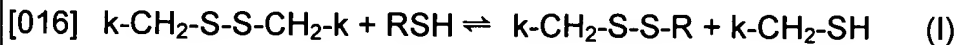
[012] While "no lye" relaxers may not contain lye, they may, however, rely on the soluble hydroxides of inorganic metals, such as potassium hydroxide and lithium hydroxide. Other "no lye" relaxers may use hydroxide ions obtained, for example, from a slightly-soluble source, such as  $\text{Ca}(\text{OH})_2$ . For example, the slightly soluble  $\text{Ca}(\text{OH})_2$  may be mixed with guanidine carbonate to form guanidine hydroxide, a soluble but unstable source of hydroxide, and insoluble calcium carbonate ( $\text{CaCO}_3$ ). This reaction is driven to completion by the precipitation of  $\text{CaCO}_3$  and is, in effect, substituting one insoluble calcium salt for a slightly soluble calcium salt. Because guanidine hydroxide is unstable, the components are stored separately until the time of their use.

More commonly, reducing agents, such as thioglycolates, sulfites, cysteines and their derivatives, are used for texturizing purposes in hair straightening or relaxing compositions.

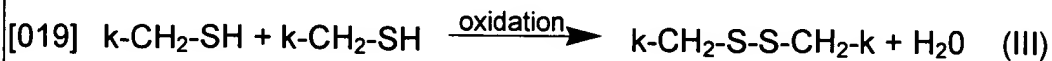
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higher the concentration of the thiolate ions in the composition, the faster the straightening or relaxing reaction will occur. See Zviak at page 190. This concentration, and therefore the rate of the reaction, are dependent on the ionization constant  $K_i$  of the thiol used. Thus, the pK value of a particular thiol expresses the nature of the thiol and determines both the equilibrium level and, therefore, the concentration of thiolate ions at a given pH. For example, reducing agents are generally used in a concentration of about 5% at a pH ranging from 9 to 10.

[015] The reducing step is generally a reversible reduction reaction of disulfide bonds within a keratin fiber which can be represented by the following reaction scheme, wherein k represents the keratin protein chain of a keratin fiber, and RSH represents a thiol containing reducing agent:



[018] Generally, the disulfide product, RS-SR, and any residual reducing agent, RSH, are rinsed from the hair, and then the disulfide bonds are restored in the neutralizing step. The neutralizing step can be represented by the following reaction scheme:



[020] These reducing agents may have disadvantages not present with alkaline agents. As described above, thiol-based relaxing may require the use of an oxidizing neutralizer, such as hydrogen peroxide, to chemically relink the hair

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[021] Some strides have been made to improve to the condition of sodium hydroxide-straightened hair by incorporating an auxiliary hair keratin disulfide reducing agent having a sulfhydryl functional group available chosen from cysteine, homologs of cysteine, and water soluble derivatives of cysteine. See, e.g, U.S. Pat. No. 4,992,267, the disclosure of which is incorporated herein by reference. This patent discloses the use of sodium hydroxide at concentrations of between about 1 weight percent to about 2.5 weight percent, such as between about 1.5 weight percent and about 2.25 weight percent relative to the total concentration of the composition.

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[023] The use of certain reducing agents and certain hydroxide-based compounds has previously been disclosed. A curing method for permanent hair straightening using thioglycolic acid, dithioglycolic acid, and potassium hydroxide is known. See Ogawa, S. et al., J. Cosmet. Sci., 51, 379-399 (2000). This method comprises three steps: (1) reduction using thioglycolic acid (3% to 9%), dithioglycolic acid, potassium hydroxide (1.05%), EDTA and monoethanolamine; (2) heat treatment, followed by (3) oxidation of the hair. Further, for example, a process for imparting smoothness, body and a permanent wave pattern is also known. See U.S. Patent No. 6,058,943. This process comprises at least eleven steps such as applying an aqueous alkaline relaxant composition containing an alkaline hydroxide reducing agent to the hair (step "(a)"), applying an aqueous waving composition containing a thioglycolate reducing agent to the hair (step "(d)"), and shampooing and rinsing the hair with a neutralizing shampoo and water (step "(h)").

[024] The present invention relates to a method for relaxing keratin fibers without damaging the fibers but at the same time without substantial reversion to the original curly state of the hair using compositions comprising low concentrations of at least one hydroxide compound and compositions comprising at least one reducing agent. Further, lanthionizing processes which allow re-waving of relaxed hair are disclosed. Hair which has been relaxed using currently available reducing agents cannot thereafter be permed because the disulfide bonds in the hair have been irreversibly altered by the lanthionizing treatment.

[025] Thus, the present invention provides, in one embodiment, a method for lanthionizing keratin fibers to achieve relaxation of the keratin fibers comprising (i)

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[026] The present invention also provides a method for re-waving keratin fibers comprising (i) applying a pretreatment composition, wherein the pretreatment composition comprises at least one reducing agent chosen from thiols, sulfites, and derivatives thereof to keratin fibers for a sufficient period of time to reduce at least one keratin bond in the keratin fibers; (ii) rinsing the keratin fibers; (iii) generating hydroxide ions in at least one solvent, wherein the step of generating comprises including at least one hydroxide compound in the at least one solvent; (iv) applying a composition comprising the generated hydroxide ions to the pre-treated keratin fibers for a sufficient period of time to lanthionize at least one of the keratin fibers; (v) heating the keratin fibers; (vi) terminating the lanthionization, and (vii) applying a permanent waving composition to the lanthionized keratin fibers for a sufficient period of time to permanently wave the keratin fibers.

[027] Further, the present invention also provides for a multicomponent kit for lanthionizing keratin fibers, wherein the kit comprises at least two compartments. A first compartment of the kit contains at least one hydroxide compound, and a second compartment contains at least one reducing agent chosen from thiols, sulfites, and derivatives thereof.

[028] The present invention also provides for a multicomponent kit for re-waving keratin fibers, wherein the kit comprises at least three components. A first compartment contains at least one hydroxide compound; a second compartment contains at least one reducing agent chosen from thiols, sulfites, and derivatives thereof; and a third compartment contains a permanent waving composition.

[029] Certain terms used herein are defined below:

[030] As used herein, "at least one" means one or more and thus includes individual components as well as mixtures/combinations.

[031] "Keratin fibers" as defined herein may be human keratin fibers, and may be chosen from, for example, hair.

[032] "Heating" refers to the use of elevated temperature (*i.e.*, above 100°C). In one embodiment, the heating in the inventive method may be provided by directly contacting the keratin fibers with a heat source, *e.g.*, by heat styling of the keratin fibers. Non-limiting examples of heat styling by direct contact with the keratin fibers include flat ironing, and curling methods using elevated temperatures (such as, for example, curling with a curling iron and/or hot rollers). In another embodiment, the heating in the inventive method may be provided by heating the keratin fibers with a heat source which may not directly contact the keratin fibers. Non-limiting examples

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[037] Thus, the present invention provides, in one embodiment, a method for lanthionizing keratin fibers to achieve relaxation of the keratin fibers comprising (i)

applying a pretreatment composition comprising at least one reducing agent chosen from thiols, sulfites, and derivatives thereof to keratin fibers for a sufficient period of time to reduce at least one keratin bond in the keratin fibers; (ii) rinsing the keratin fibers; (iii) generating hydroxide ions in at least one solvent, wherein the step of generating comprises including at least one hydroxide compound in the at least one solvent; (iv) applying a composition comprising the generated hydroxide ions to the pre-treated keratin fibers for a sufficient period of time to lanthionize at least one keratin fiber; (v) heating the keratin fibers; and (vi) terminating the lanthionization when the keratin fibers are relaxed. In one embodiment, the method further comprises shampooing the keratin fibers subsequent to heating the keratin fibers. The method may further comprise rinsing the keratin fibers prior to and/or subsequent to shampooing the keratin fibers.

[038] The present invention also provides a method for re-waving keratin fibers comprising steps (i) to (vi) above, and then (vii) applying a permanent waving composition to the lanthionized keratin fibers for a sufficient period of time to permanently wave at least one keratin fiber. In one embodiment, the method further comprises rolling the lanthionized keratin fibers onto at least one curling rod after prior to or following the application of the permanent waving composition. In another embodiment, the method further comprises rinsing the rolled keratin fibers after a sufficient period of time to permanently wave at least one of the rolled keratin fibers.

[039] Further, the present invention also provides for multicompartment kits for lanthionizing or re-waving keratin fibers. The lanthionizing kit comprises at least two

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compartments. A first compartment of the kit contains at least one hydroxide compound, and a second compartment contains at least one reducing agent chosen from thiols, sulfites, and derivatives thereof. The re-waving kit comprises at least three compartments. A first compartment contains at least one hydroxide compound; a second compartment contains at least one reducing agent chosen from thiols, sulfites, and derivatives thereof; and a third compartment contains a permanent waving composition.

[040] Not to be limited to theory, the inventors believe that, by using a pretreatment composition comprising at least one reducing agent, the reducing reaction may be confined to the formation of a cysteine residue,  $k\text{-CH}_2\text{-SH}$ , and the mixed disulfide,  $k\text{-CH}_2\text{-S-S-R}$ , (*i.e.*, Equation (I)). Thus, when the keratin fibers are rinsed following a sufficient time to allow the at least one reducing agent to penetrate the keratin fiber, the reducing reaction (*i.e.*, Equation (I)) may be largely reversed, leaving low concentrations of the mixed disulfide and the cysteine residue. Thus, the relaxing capability of the composition comprising at least one hydroxide compound (which is subsequently applied) may be increased by breaking at least some of the cystine disulfide bonds in the keratin fibers and forming the cysteine residue using the pretreatment composition, and by the use of heat. Thus, the heat and the presence of the cysteine residues may catalyze the rearrangement of the protein rearrangement and lanthionization within a keratin fiber. Therefore, low concentrations of the at least one hydroxide compound may be sufficient to effect relaxation of the keratin fibers. Further, the use of the pretreatment composition comprising at least one reducing agent may result in fewer lanthionine cross-links

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[041] According to the present invention, the at least one hydroxide compound may be chosen from any compound comprising at least one hydroxide group which may at least partially dissociate into a counterion and a hydroxide ion in solution.

hydroxide may be formed *in situ*, for example, from the reaction of calcium hydroxide and guanidine carbonate.

[043] The at least one reducing agent of the present invention is chosen from thiols, sulfites, and derivatives thereof. As used herein, derivatives include salts. The at least one reducing agent may be chosen from thiols, sulfites and derivatives thereof such as, for example, those listed in the International Cosmetic Ingredient Dictionary and Handbook, 8<sup>th</sup> Ed., Vol. 2 (2000) at page 1767. Non-limiting examples of suitable thiols are thioglycolates, thiolactates, thioglycerols, thiocarboxylic acids, thioesters, thioamides, alkyl mercaptans, and cysteines. In one embodiment, the at least one reducing agent is chosen from thioglycolates, and in yet another embodiment, the at least one reducing agent is monoethanolamine thioglycolate. Non-limiting examples of suitable sulfites are hydrogen sulfite, organic sulfites such as alkyl sulfites (such as dimethyl sulfite and diethyl sulfite) and alkylene sulfites (such as glycol sulfite, 1,2-propyleneglycol sulfite, and 1,3-butyleneglycol sulfite), and inorganic sulfites (such as ammonium sulfite, magnesium hydrogen sulfite, potassium sulfite, sodium sulfite, sodium hydrogen sulfite, silver sulfite, and zinc sulfite).



[045] Permanent waving compositions useful in the present invention may be chosen from any known permanent waving composition. Further, according to the present invention, the at least one solvent can be chosen from solvents commonly used in compositions for the hair. Non-limiting examples of the at least one solvent include water and solvents which may lower the ionic bonding forces in the solute molecules enough to cause at least partial separation of their constituent ions, such as dimethyl sulfoxide (DMSO). In one embodiment, the at least one solvent is chosen from water and DMSO. The at least one solvent can be present in an amount sufficient to ensure that, upon mixing, enough of the generated available hydroxide ions remain soluble in order to effect lanthionization of keratin fibers.

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[047] The compositions of the present invention may be provided in the form of a multicompartment kit. According to one embodiment of the present invention, the multicompartment kit for lanthionizing keratin fibers may comprise at least two separate compartments. A first compartment of the kit may comprise a first composition containing at least one hydroxide compound. This first composition can be in a form chosen from an emulsion, suspension, solution, gel, cream, and a paste. A second compartment of the kit can comprise a pretreatment composition comprising at least one reducing agent. This composition may be in a form chosen from an emulsion, suspension, solution, gel, cream, and paste. The skilled artisan, based on the stability of the composition and the application envisaged, will be able to determine how the multicompartment compositions should be stored and mixed.

[049] Other than in the operating example, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used

in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should be construed in light of the number of significant digits and ordinary rounding approaches.

[050] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. The following examples are intended to illustrate the invention without limiting the scope as a result. The percentages are given on a weight basis.

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[055] **Tabl 1. Relaxing Efficiency (% RE) of Hair Tr at d with Thioglycolate Solutions at Diff rent pHs and with Various Sodium Hydroxide Solutions**

pH of Composition Comprising 5% MEA- TGA	Amount of NaOH (%)			
	0.3	0.5	0.7	1.0
5.2	62%	64%	71%	87%
7.0	63%	68%	86%	89%
9.0	89%	91%	95%	96%

[056] A high relaxation efficiency after 24 hours under 90% relative humidity indicates that the hair did not display reversion. Thus, the data show that hair can be effectively relaxed without substantial reversion after being treated with a solution containing a low concentration of monoethanolamine thioglycolate and a solution containing a low concentration of NaOH and then subjected to heat. Monoethanolamine thioglycolate solutions having a higher pH resulted in a higher relaxation efficiency.

[057] **Example 2. The Effect of the Concentration of Thioglycolate Solution on the Relaxing Efficiency**

[058] Following the above procedure, natural ethnic hair was treated first with a solution containing an amount of MEA-TGA as shown in Table 2 having pH 9.0 for 10 minutes, then with a solution containing an amount of sodium hydroxide as shown in Table 2, and then the relaxing efficiency was determined. The results are shown in Table 2.

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Amount of MEA-TGA (%)	Amount of NaOH (%)			
	0.3	0.5	0.7	1.0
1	50%	63%	68%	79%
3	80%	83%	87%	96%
5	89%	91%	95%	96%

**[061] Example 3. The Effect of the Length of Time for Treatment with a Thioglycolate Solution on the Relaxing Efficiency**

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Length of Treatment Time (seconds)	Relaxing Efficiency (%RE)
60	50%
90	60%
120	82%

**[065] Example 4. Permability of Relaxed Hair**

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placed in a humidity chamber at 90% relative humidity for at least 24 hours. The percent Perming Efficiency (%PE) is defined as:

$$\%PE = (L_r/L_p) \times 100$$

where  $L_p$  = length of the permed hair after 24 hours at 90% RH

$L_r$  = length of the hair before the perm

[067] The greater the perming efficiency (% PE), the curlier the hair after perming.

The results are shown in Table 4.

[068] **Table 4. Perming Efficiency (%PE) of Hair Treated with a Thioglycolate Solution, a Sodium Hydroxide Solution, Heat and then Permed**

	Control	Amount of NaOH in Sodium Hydroxide Solution (%)			
		0.3	0.5	0.7	1.0
%PE	22%	62%	64%	52%	50%

[069] The high perming efficiency after 24 hours under 90% relative humidity indicates that the hair relaxed using the inventive method prior to perming is permable. Hair relaxed using a commercially available lye relaxer prior to perming displayed poor perming efficiency.

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